ANALYSIS OF A SYSTEM TO THERMALLY DISSOCIATE WATER USING A SEMI-PERMEABLE MEMBRANE

by

N. C. Ford, Jr.

U of C-AUA-USERDA

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

ANALYSIS OF A SYSTEM TO THERMALLY DISSOCIATE WATER

USING A SEMI-PERMEABLE MEMBRANE

by

N. C. Ford, Jr.

ABSTRACT

A scheme using oxygen and hydrogen permeable membranes to thermally dissociate water into hydrogen and oxygen in order to provide for the storage and transportation of thermal energy is described and analyzed in terms of presently available materials. While the process is potentially very efficient, the membranes required to separate the hydrogen and oxygen are not stable at sufficiently high temperatures. It is concluded that a high temperature hydrogen permeable membrane must be discovered before further work is warranted. The rare earth-palladium compounds may have the desired characteristics.

I. INTRODUCTION

The use of solar energy to fuel central power stations depends upon our ability to store energy for use during the night and periods of cloudy weather. In addition, it may prove desirable to locate large scale solar collectors in the desert in order to take advantage of the lower average cloud cover. If this is done, energy must be transported over long distances to centers of use. One of the most attractive solutions to both of these problems - the storage and the transportation of energy - may be found in the dissociation of water to give hydrogen which may in turn be used as a fuel.

It is possible to accomplish this goal with presently available technology. Electricity generated using a steam turbine can in turn be used to electrolyze water yielding hydrogen and oxygen. Unfortunately, this process involves a number of steps and will almost certainly prove to be too expensive. Consequently, it is desirable to find a thermal dissociation process which is both efficient and inexpensive. Three types of processes may be used to provide the necessary separation of hydrogen and oxygen; those using a series of chemical reactions; those operating on the physical differences between hydrogen and oxygen; and those using semi-permeable membranes.

The only possibility that has received substantial attention to date is the first, the series of chemical reactions. These processes have been discussed by Abraham and Schreiner[1], de Beni and Marchetti[2], and others. They will not be considered further here.

The second type of process makes use of the lower mass of hydrogen, or of the fact that the diffusion constant of hydrogen is three times that of water, and four times that of oxygen, to perform the separations. Included in this category are diffusion membranes, vortex tubes, and jet separators[3]. All of these methods require a great deal of work to effect the separation, unless temperatures in the vicinity of $3000^{\circ}K$ are used[4], and consequently can be expected to have low efficiency.

Finally, we can make use of semipermeable membranes to dissociate water. If we heat water to temperatures in the range of 1500° to $2000^{\circ}K$, a small fraction is thermally dissociated and the oxygen and hydrogen may be withdrawn from the reaction chamber through membranes selectively

permeable to the two elements. By cooling the gases to ambient tempera-
ture before compressing them to useful pressure, the quantity of work
required to effect the overall dissociation

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g) \tag{1}$$

at atmospheric pressure and $25^{\circ}C$ may be substantially reduced. This is
of great importance in avoiding the difficulties pointed out by Funk and
Reinstrom[4] in attempting to dissociate water in a single step process at
temperatures below $3000^{\circ}K$. This report gives a detailed discussion of
the principles involved and problems encountered in designing a practical
semipermeable membrane water dissociation plant.

In Section II, we describe in greater detail the membrane
dissociation and discuss the energy balance assuming ideal components
are available. In Sections III - V, the individual components are discussed
in the light of presently known materials and techniques. Finally, in
Section VI, the energy flow in the sample system is reviewed in the light
of more realistic assumptions concerning its components and it is concluded
that the process is not now practical.

II. THE PROPOSED SYSTEM

A schematic drawing of the proposed system is shown in Fig. 1.
The entire water system is at pressure P_o, but the water is circulated
continuously between the temperatures T_1 and T_2. The two temperatures
are required because of the properties of the available membranes. Heat
transfer from the higher to lower temperature is minimized using the heat
exchanger. At the higher temperature, T_2, a fraction X of the oxygen
contained in the water is removed through an oxygen permeable membrane
at pressure P_2. The oxygen is cooled by the entering water, and compressed
to atmospheric pressure. (We consider only this pressure in order to
compare the work required in compressing the gases to the standard heat
of formation of water). The remaining water-hydrogen mixture is circulated
to temperature T_1, where the hydrogen is drawn off through a second membrane
at pressure P_1, cooled, and compressed. Enough water is added to make up
for the dissociated fraction, the water is returned to temperature T_2, and
the cycle is repeated.
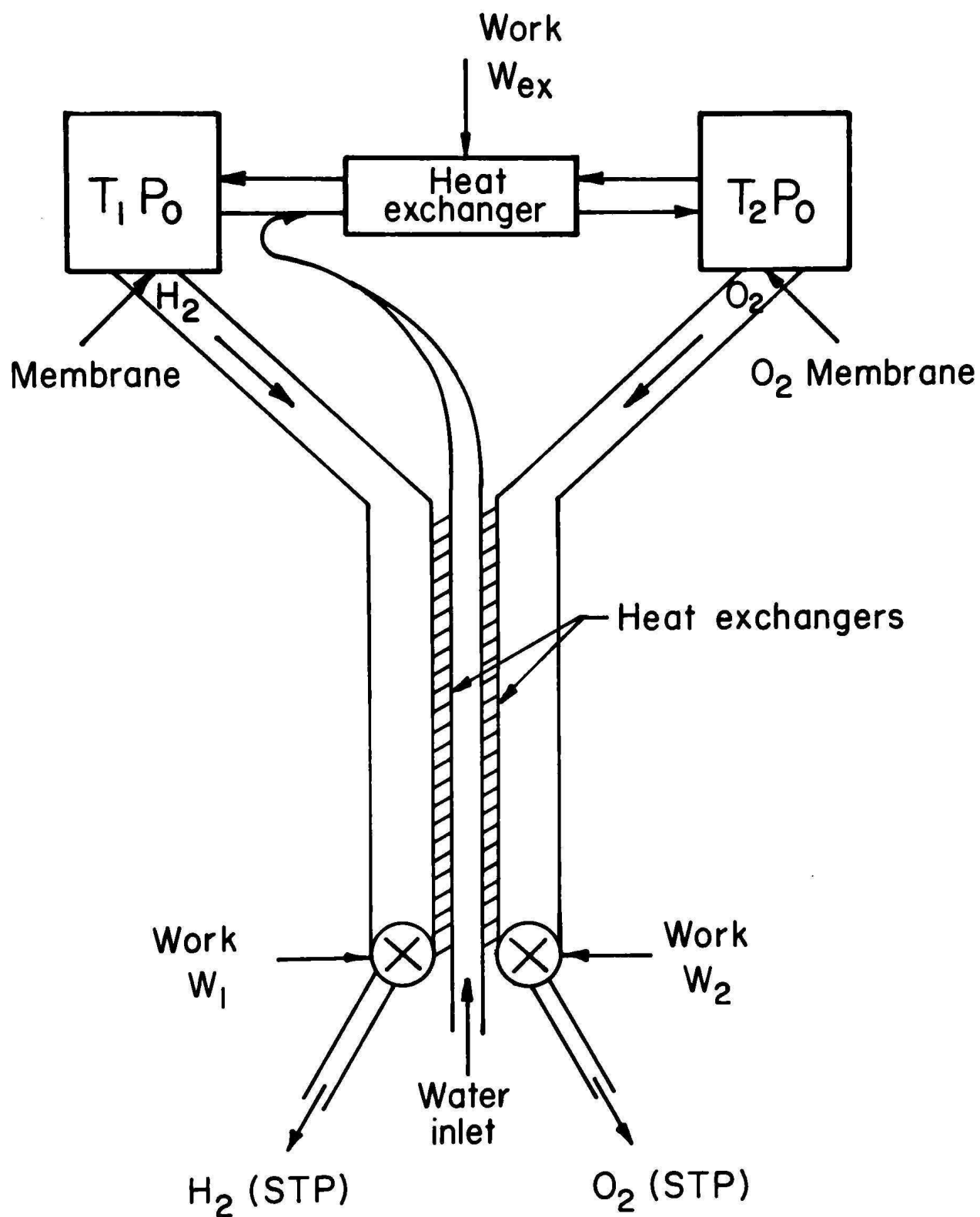
Fig. 1. Schematic Diagram of Overall Membrane Dissociation System.

If the heat exchangers are ideal, the high temperature water, as well as the hydrogen and oxygen, are assumed to be ideal gases, and the water is assumed to be incompressible, the energy balance may be easily derived. The quantity of heat required is ΔH_o, the heat of formation of liquid water (68.4 Kcal/mole), and the work which must be done on the gases to compress them when one mole of water is dissociated is

$$W = -RT_o \ln P_1 - \frac{1}{2} RT_o \ln P_2 \quad . \tag{2}$$

We have assumed the compression is isothermal at temperature T_o and the pressures P_1 and P_2 are measured in atmospheres.

We now need a relation between the oxygen pressure P_{O_2}, total pressure P_o, and fraction of water dissociated X. Notice that pressures P_{O_2} and P_{H_2} are always greater than P_2 and P_1. These pressure differences drive the gases through the membranes. Suppose we begin with one mole of water at temperature T_2, and remove $\frac{X}{2}$ moles of oxygen. The remaining mixture will still be partially dissociated. Assume there are $\frac{\alpha}{2}$ moles of oxygen. There are as a result $1-X-\alpha$ moles of water, and $X + \alpha$ moles of hydrogen. The mole fractions of the three constituents, X_{H_2O}, X_{H_2}, and X_{O_2} are consequently

$$X_{H_2O} = (1 - X-\alpha)/(1 + \alpha/2) \quad , \tag{3a}$$

$$X_{H_2} = (X + \alpha)/(1 +\alpha/2) \quad , \tag{3b}$$

$$X_{O_2} = \frac{\alpha}{2} / (1 + \alpha/2) \quad , \tag{3c}$$

where the denominators are required to make the sum of the three quantities equal to 1. We insert these quantities into the law of mass action evaluated at temperature T_2

$$\frac{X_{H_2O}}{(X_{H_2}) (X_{O_2})^{1/2}} = P_o^{1/2} K(T) \tag{4}$$

5

and make use of the ideal gas assumption

$$P_i = X_i P_o \quad , \tag{5}$$

to obtain the expression

$$K(T) = \frac{(1-X-\alpha)}{(X+\alpha)\ (P_{O_2})^{1/2}} \quad . \tag{5a}$$

Finally we solve Eq. 3c for α using Eq. 5,

$$\alpha = \frac{2P_{O_2}}{P_o - P_{O_2}} \quad , \tag{5b}$$

and use this result in Eq. 5a to obtain

$$X = \frac{1}{1 + K(T)(P_{O_2})^{1/2}} - \frac{2P_{O_2}}{P_o \quad P_{O_2}} \quad , \tag{6a}$$

which may also be written

$$X = (P_{H_2} - 2P_{O_2})/(P_o - P_{O_2}) \quad . \tag{6b}$$

The necessary work of compression assuming zero pressure drop across the membranes is easily found if we assume the oxygen pressure at T_1 is negligible, a valid assumption if $T_1 << T_2$, and is given by

$$W = -R\ T_o \ln X\ P_o - \frac{1}{2} R\ T_o \ln P_{O_2} \quad . \tag{7}$$

In the limit $P_o >> P_{H_2} >> 2\ P_{O_2}$ Eq. 6b becomes $X = P_{H_2}/P_o$ and, with Eq. 4

$$W = + R\ T_o \ln [K(T_2)/P_{H_2O}] \quad , \tag{8}$$

but for all practical purposes $P_{H_2O} = P_o$, and we can use the approximation[5]

$$K(T) = 10^{-3} \exp (6 \times 10^4/RT) \tag{9}$$

whence

$$W = 6 \times 10^4 \frac{T_o}{T_2} - (6.91 + \ln P_o) RT_o \quad . \qquad (10)$$

Eq. 10 shows clearly the advantage of compressing the gases at low temperature T_o rather than at the dissociation temperature T_2. It is the ratio T_o/T_2 in the first term that allows this water dissociation scheme to avoid the arguments of Funk and Reinstrom[4]. If $T_o = 300^\circ K$, $T_2 = 1800^\circ K$ and $P_o = 1$ atm, Eq. 10 shows the work needed to compress H_2 and O_2 is 5.85 Kcal/mole dissociated. This is small enough to be a reasonable energy expense when compared to the energy required for dissociation, 68.4 Kcal/mole. We conclude the ideal system has a satisfactory energy balance.

Before leaving the ideal system, it is necessary to discuss briefly the problems associated with pumping large quantities of gases at low pressures. For each 10^3 watts of input heat, 3.5×10^{-3} moles of water will be dissociated each second. Thus, 7.8×10^{-2} liters of H_2 and 3.9×10^{-2} liters of O_2 at STP will be produced each second. The pumping capacity must therefore be, with pressures in atmospheres,

$$C = \frac{7.8 \times 10^{-2}}{P_{H_2}} + \frac{3.9 \times 10^{-2}}{P_{O_2}} \qquad (11)$$

liters/sec – Kw at the low pressures. The price of large volume vacuum pumps is within a factor of two of $5 per liter/sec. Thus, it is not practical to compress the gases by a factor of more than 100 because the pump costs alone would then exceed $58.40/Kw dissociated, an unacceptably high figure. We adopt a criteria of minimum adequate pressure $P_{min} = 10^{-2}$ atmospheres.

A second limit to P_{min} might be considered: that imposed by the pumping speed of the pipe connecting the dissociation furnace to the vacuum pump. Assume the pipe has radius r and length L. Then, the pressure drop along the pipe is

$$\Delta P = f\left(\frac{L}{2r}\right) \left(\frac{1}{2}\rho v^2\right) \quad ,$$

where f is a friction coefficient given by

$$f = \frac{64}{N_{Re}}$$

for laminar flow and approximately by

$$f = \frac{0.3164}{(N_{Re})^{1/4}}$$

for turbulent flow[6]. N_{Re} is the Reynolds number

$$N_{Re} = \frac{2vr\rho}{\eta} \quad,$$

ρ the gas density, v its velocity, and η its viscosity. The units must be consistent; for example, we can use P in dynes/cm^2, ρ in gms/cm^3, v in cm/sec and η in poise. Assuming turbulent flow, we find for the pipe radius

$$r \cong \left[\frac{6.75 \times 10^5 \, L \, M^{7/4} \eta^{1/4} \, T_{ave}}{P \, \Delta P \, M_w}\right]^{0.21} \tag{12}$$

where $T_{ave} = \frac{T_2 + T_o}{2}$, M is the mass flow in gms/sec and M_w is the molecular weight of the gas. For example, if M = 7 gms/sec (corresponding to the hydrogen production for a 10^6 watt installation), $\eta = 3 \times 10^{-4}$ poise, $T_{ave} = 10^3$ °K, P = 10^4 dyne/cm^2 (10^{-2} atm), P = 10^3 dyne/cm^2 (10^{-3} atm) and M_w = 2, we find for a 10^2 cm long pipe r = 4.5 cm, a satisfactory dimension. If we assume ΔP is proportional to P, the pipe size scales as $[P]^{-0.42}$ and a further reduction by a factor of at least 10 in P would be permissible. We conclude that the pump costs, rather than pipe sizes, remain the limiting factor on P_{min} .

It is instructive to convert the criteria $P_{min} = 10^{-2}$ atm into a relationship between T_2 and the minimum allowed value of P_o. From Eq. 4 we have, setting $P_{H_2} = P_{O_2} = 10^{-2}$ atm

$$P_o \geq 10^{-6} \exp [6 \times 10^4 / RT] \quad. \tag{13}$$

This equation is plotted in Fig. 2. The regions of temperature and pressure in which it may be practical to operate a dissociation apparatus is indicated. As we shall see later, a practical installation can approach these conditions only if $T_1 = T_2$. The requirements of the heat exchanger when separate temperatures are used leads to more severe operating conditions.
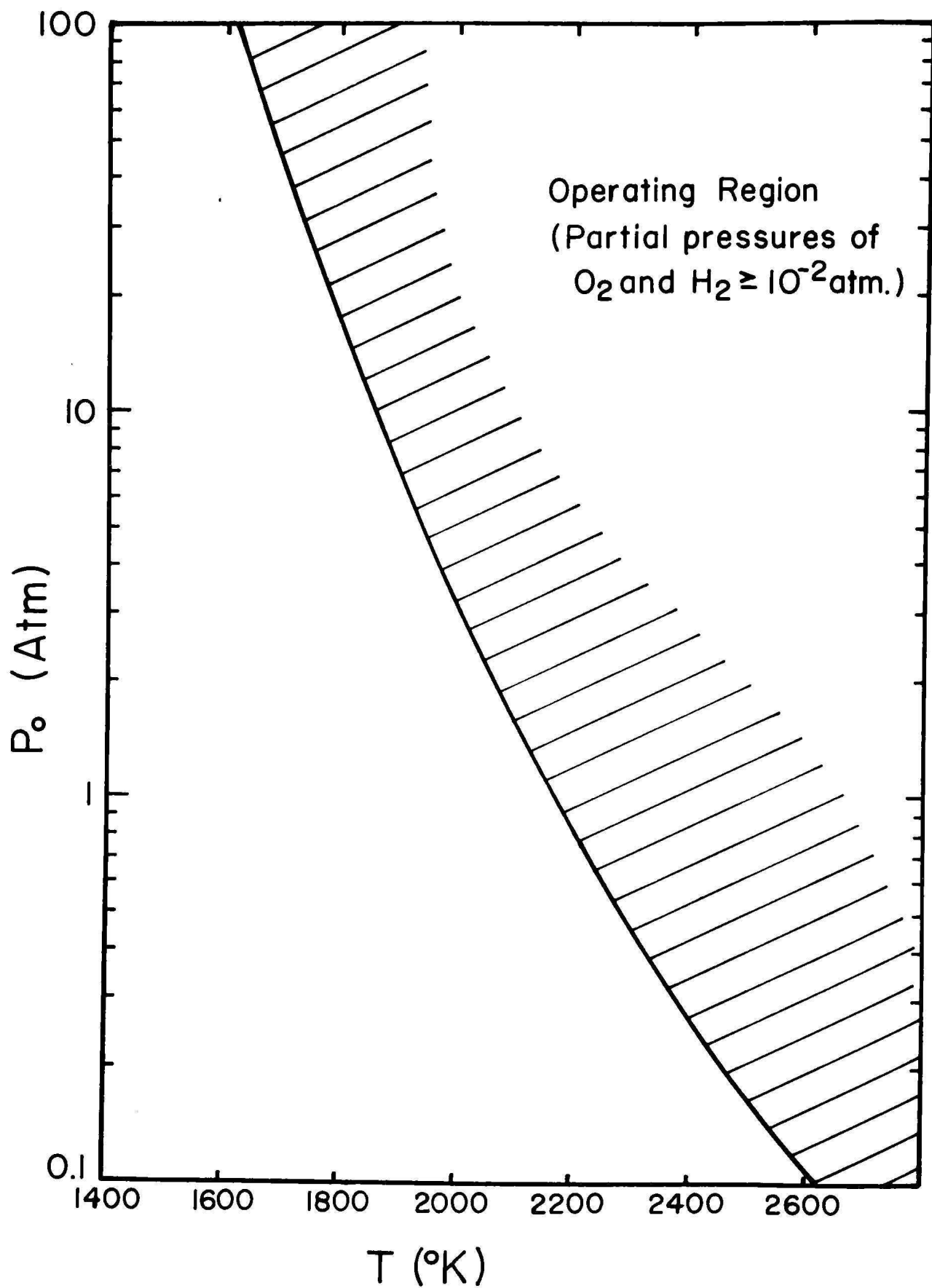
Fig. 2. Minimum Total Pressure at Which System Can
Be Operated as Function of Temperature.

III. THE HYDROGEN MEMBRANE

The extraordinary permeability of palladium to hydrogen was discovered in 1866 by Thomas Graham. Studies of the H_2 - Pd system are summarized in books by Wise[7] and Lewis[8] and in a series of articles by various authors in the Englehard Industries Technical Bulletin[9]. A number of patents describe techniques for the production of hydrogen using a Pd membrane[10], and commercial units are available from Matthey Bishop, Inc. of Malvern, Pa. providing up to 1500 ft^3 (STP) of pure hydrogen per hour from dissociated ammonia.[11] The commercial units use an alloy of about 23% silver in palladium for the membrane. This alloy has mechanical and hydrogen permeability properties superior to those of pure palladium. We note for comparison that a 150,000 watt dissociation unit would produce about 1500 ft^3/hour of hydrogen.

The permeability of palladium to hydrogen has been discussed by a number of authors[12-18]. The results vary from author to author, but within 20% can be expressed by the relation

$$J = \frac{5 \times 10^{-7} A}{t} \quad (P_2^{1/2} - P_1^{1/2}) \exp (-3200/RT) \tag{14}$$

where J is the flux of hydrogen in moles/sec through a membrane of area A cm^2 and thickness t cm. P_1 and P_2 are the hydrogen pressures in atmospheres.

From Eq. 14 we see that it is advantageous to operate the H_2 membrane at the highest possible temperature. The temperature in practice is limited by the rate at which palladium is lost by evaporation. The vapor pressure of Pd is well represented by the equation[19]

$$V_p = 1.31 \times 10^6 \exp [-46,500/T] \text{ atm.} \tag{15}$$

Using this equation in the expression for the loss of material in vacuum[19],

$$G = 1.01 \times 10^6 \, V_p \sqrt{\frac{M_w}{2\pi RT}} \quad \text{gms/sec } cm^2 \tag{16}$$

where M_w is the molecular weight, and converting to the more convenient unit of cm/year lost from the membrane Δt, we find

$$\Delta t = \frac{1.55 \times 10^{15} \exp(-46500/T)}{\sqrt{T}} \text{ cm/year} \quad . \tag{17}$$

Several values of this quantity are given in Table I. It is clear that

TABLE I. Palladium Loss Rates as a Function of Temperature

$T^\circ K$	Δt cm/year
1000	4.9×10^{-7}
1100	3.08×10^{-5}
1200	1.12×10^{-3}
1300	1.94×10^{-2}
1400	2.28×10^{-1}
1500	2.00

temperatures in excess of $1100^\circ K$ cannot be tolerated. (It is true that the loss rate would be greatly reduced by the presence of a stationary gas, but in practice, the water vapor-hydrogen mixture must flow in order to provide for the continuous renewal of hydrogen rich gas. The loss rate as calculated here represents an upper limit, but is probably realistic.) It is possible that this temperature could be raised by almost 200° using one of the rare eath - Pd compounds with melting points given in Table II[20]. The hydrogen permeability of these compounds is not known, however, and may be too small to be practical.

TABLE II. Melting Point of Rare Earth-palladium Compounds

Compound	Melting Point
Pd(pure)	$1552^\circ C$
YPd_3	1700
$GdPd_3$	1630
$SmPd_3$	1620
$DyPd_3$	1710
$HoPd_3$	1730
$ErPd_3$	1710

If we assume $P_1 = 1/2 \, P_2 = 10^{-2}$ atm and $T = 1100^\circ K$, we find from Eq. 14

$$J = 0.35 \times 10^{-8} \, \frac{A}{t} \text{ moles/sec.} \tag{18}$$

Since the hydrogen production is 3.5×10^{-3} moles/Kw-sec, we see that the area of the membrane must be

$$A = 10^6 \, t \text{ cm}^2/\text{Kw} . \tag{19}$$

and the quantity of Pd required is $m = \rho A t = 12 \times 10^6 \, t^2$ gms/Kw. A membrane 10^{-4} cm thick would use a reasonable quantity of Pd providing it could be manufactured and supported. It could, for example, be supported by a porous ceramic form to avoid rupturing. It may be possible to fill the pores of the ceramic form with a low melting point metal, evaporate the Pd film onto the form, and then remove the second metal by heating in the presence of a H_2 pressure differential.

Even if the above technique is successful, an additional problem may be encountered. The Pd permeability as measured in the past has always been limited by the diffusion of H_2 in the metal. No evidence has been obtained to suggest that the rate of solution of H_2 in Pd provides a limitation to the permeability. However, for sufficiently thin membranes the solution rate must be the limiting process; at present, it is not known what process will limit the permeability of a 10^{-4} cm thick membrane.

IV. THE OXYGEN MEMBRANE

Many of the metal oxides are selectively permeable to oxygen. Of these, two have been considered for use in the water dissociation scheme: stabilized zirconia and urania. We take up zirconia first.

Pure zirconia undergoes a crystalline phase change at about $1400^\circ K$ which leads to mechanical failure upon temperature cycling through that temperature. However, additions of calcia, yttria, or magnesia will stabilize the crystal structure against temperature cycling. The oxygen permeability of two of these materials, calcia[21] and yttria[22] stabilized

zirconia have been measured. The results may be expressed as

$$J = 1.35 \times 10^{-2} \exp\ [-55,700/RT]\ \frac{A}{t}\ (P_2^{1/2} - P_1^{1/2})\ \text{moles/sec} \quad (20)$$

for calcia stabilized zirconia and

$$J = 4.3 \times 10^{-2} \exp\ [-57,600/RT]\ \frac{A(P_2^{1/2} - P_1^{1/2})}{t}\ \text{moles/sec} \quad (21)$$

for yttria stabilized zirconia. Again, pressures are measured in atmospheres and dimensions in cm. The dependence on $P^{1/2}$ for the calcia stabilized material is questionable. Smith, et al[21] reports a $P^{1/4}$ dependence, but the data shown seems to fit the $P^{1/2}$ dependence equally well. In any event, over the pressure range of 6×10^{-3} to 120×10^{-3} atmospheres O_2 pressure the error is at most 50%. The $P^{1/2}$ dependence is well obeyed in the yttria-zirconia.

The vapor pressure of ZrO_2 is given by[22a]

$$V_p = 7.6 \times 10^7 \exp\ [-82,500/T]\ \text{atm.} \quad (21a)$$

If this is the only zirconium containing vapor, the loss rate will be

$$\Delta t = \frac{2.03 \times 10^{17} \exp\ [-82,500/T]}{\sqrt{T}}\ \text{cm/year.} \quad (21b)$$

TABLE III. Loss Rates for ZrO_2

T $^\circ$K	Δt cm/year
1800	4.8×10^{-5}
1900	4.65×10^{-4}
2000	4.55×10^{-3}

Some values are shown in Table III. It is practical to use an operating temperature of 1800° with a 10^{-4} cm membrane. The membrane would have to be renewed about once a year.

It is possible that the compound $Zr(OH)_4$ will also have an appreciable partial pressure in the presence of H_2O[22b]. It would be

formed by the reaction

$$ZrO_2 + 2H_2O \longrightarrow Zr(OH)_4 \qquad (21c)$$

and could considerably enhance the loss rate from a ZrO_2 membrane. At the present time, it is not possible to estimate the importance of this reaction.

The behavior in urania is rather more complex because the solubility of oxygen in UO_2 to form UO_{2+x} is very large and non-ideal. To calculate the permeability of a membrane we require first the solubility of oxygen in UO_2 as a function of oxygen pressure S(P) and second, the chemical diffusion constant D. The flux of oxygen through the membrane will then be given by

$$J = \frac{A}{t} D [S(P_2) - S(P_1)] \quad . \qquad (22)$$

If S is measured in moles/cm^3, the flux will be in moles/sec. Care must also be exercised that the chemical diffusion constant D be used rather than the self-diffusion constant D_o^*. The two are related by the equation[23]

$$D = D_o^* \left(\frac{2+x}{x}\right) \left(\frac{1}{2} \frac{d \ln P_{O_2}}{d \ln x}\right) \quad . \qquad (23)$$

In this equation x is the number of excess oxygen atoms per uranium atom.

For the dependence of x on P_{O_2}, we refer to the data of Anthony, et. al.,[24] and Hagemark and Broli[25] which may be represented over the region of interest (x = 0.1 to 0.2) by the expression

$$\ln P_{O_2} = 70x - \frac{32,900}{T} - 1.05 \quad . \qquad (24)$$

The diffusion constant measurements show a dependence upon the deviation from stoichiometry as was theoretically predicted by Thorn and Winslow[26] but of even greater magnitude. Recent measurements have been reviewed by Belle[27] and additional results are given by Marin and Contamin[28] and Lay[29]. As shown in Fig. 3, the results for x in the range of 0.1 to 0.2
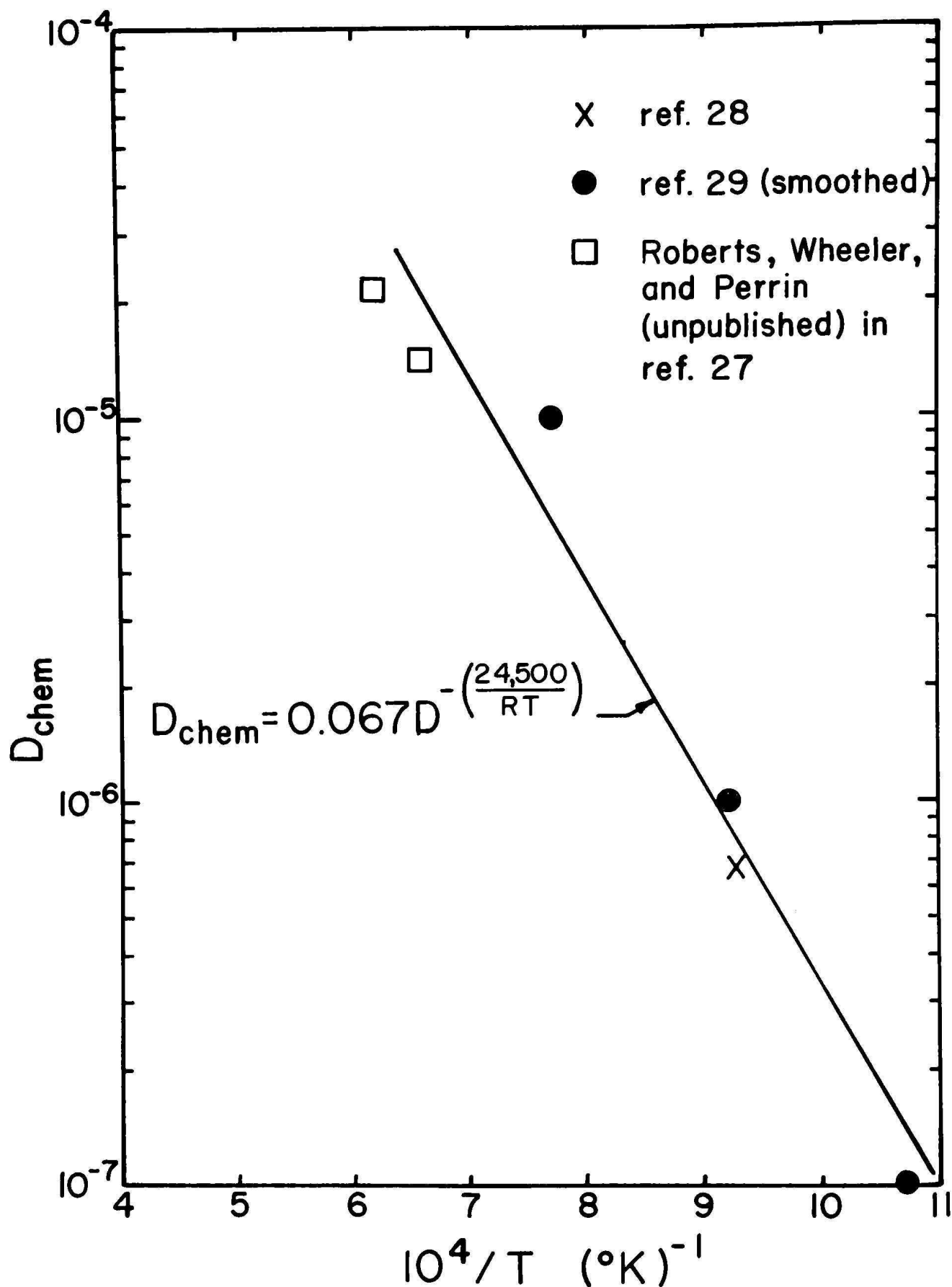
Fig. 3. The Chemical Diffusion Constant vs $10^4/T$ for UO_2.

are reasonably represented by

$$D = 0.067 \exp (-24,5000/RT) \quad . \tag{25}$$

The relation between the solubility in moles/cm^3 and x is $S = 2.04 \times 10^{-2}$ x so that from Eqs. 22, 24, and 25 we find

$$J = 1.95 \times 10^{-5} \exp (-24,500/RT) \ln \left(\frac{P_2}{P_1}\right) \frac{A}{t} \text{ moles/sec.} \tag{26}$$

We notice that the oxygen flux depends upon the pressure ratio rather than a pressure difference as for the other membranes we have discussed. This feature makes the UO_{2+x} membrane particularly attractive for use with low pressure. Unfortunately, the material loss rate prevents the use of the UO_{2+x} membrane at the necessary temperatures. The vapor above UO_2 is, under oxygen rich conditions, almost entirely in the form of UO_3. Blackburn[30] gives approximate expressions for the vapor pressure of UO, UO_2, and UO_3. The result for UO_3 is, assuming it is the only uranium oxide in the vapor,

$$V_p = \exp (-45,200/T + 16.2) \quad . \tag{27}$$

This pressure would result in an unacceptably large loss rate at temperatures above 1000°K. Consequently, despite the very attractive features of the UO_2 oxygen membrane, it cannot be employed in this dissociation scheme.

V. HEAT EXCHANGERS

If the oxygen and hydrogen are to be removed at different temperatures, and only a small fraction of the water can be dissociated during a single cycle, it becomes necessary to use a regenerative heat exchanger in order to avoid excessive transport of heat from the higher to lower temperature. The design of the heat exchanger is of critical importance in determining the efficiency of the system and consequently warrants careful discussion.

Fig. 4 shows schematically the heat exchanger. It will, of course, operate in the counterflow mode. Let us assume for the sake of simplicity
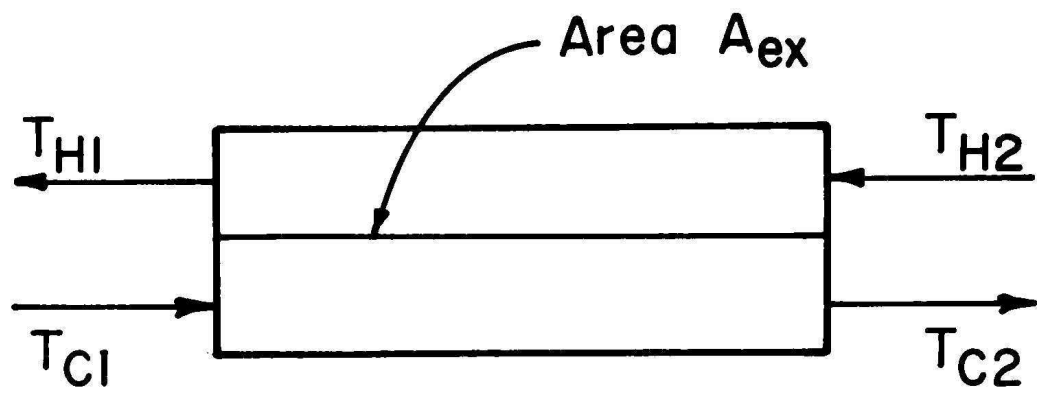
Fig. 4.   Schematic Diagram of the Heat Exchanger.

that the specific heat of water C_p is independent of temperature. We then have, setting $\Delta T = T_{H2} - T_{C2} = T_{H1} - T_{C1}$, that the net transport of heat is given by

$$q = MC_p \ \Delta T \ \text{cal/sec} \ ,$$

where M is the mass flow rate in gm/sec. If a fraction X of the water is dissociated each cycle the quantity of heat consumed in dissociation is $\frac{M}{18} X \Delta H_o$ and the fraction of heat used is dissociation ε is

$$\varepsilon = \cfrac{1}{1 + \cfrac{18 C_p \Delta T}{X \Delta H_o}} \ . \tag{29}$$

The remaining heat (a fraction $1 - \varepsilon$ of the original heat) is rejected at the lower temperature and may, of course, be used for other purposes such as generating electricity. The dissociation may thus be considered as a topping cycle.

The exchanger itself is described by the exchange area A_{ex} and the overall heat transfer conductance U. The heat exchanged each second is $UA_{ex}\Delta T$ so that

$$MC_p(T_{H2} - T_{H1}) = UA_{ex}\Delta T \ . \tag{30}$$

It is also necessary to know the work necessary to operate a unit area of the heat exchanger, W_{ex}. For any given geometry of heat exchanger there is a unique relation between U and W_{ex} for a gas of specified properties. Kays et.al.[31] have tabulated results for a number of geometries and McAdams[32] has summarized their conclusions. They presented the data for air at one atmosphere pressure and $500^o F$ ($533^o K$). To convert the data to other conditions the equations

$$U = U_{std} \left(\frac{C_p}{C_{p\,std}}\right) \left(\frac{\eta}{\eta_{std}}\right) \left(\frac{N_{Pr\,std}}{N_{Pr}}\right)^{2/3} \ ,$$

$$W_{ex} = W_{ex\,std} \left(\frac{\rho_{std}}{\rho}\right)^2 \left(\frac{\eta}{\eta_{std}}\right)^3 \tag{31}$$

are used. Here η, ρ, and N_{Pr} are the viscosity, density, and Prandtl numbers of the gas in question.

It is probably possible to build an exchanger with $U_{std} = 10^{-3}$ cal/sec $cm^2{}^oC$, $W_{ex\,std} = 2 \times 10^{-4}$ cal/sec-cm^2 and with a surface area to volume ratio of 15 cm^2/cm^3. Based on these figures and Eq. 30,

$$U = 3.7 \times 10^{-3} \text{ cal/sec } cm^2{}^oC \quad , \tag{32(a)}$$

$$W_{ex} = \frac{7.60 \times 10^{-2}}{P_o{}^2} \quad \text{cal/sec } cm^2 \quad , \tag{32(b)}$$

and the volume V of the exchanger is

$$V = \frac{A}{15} \text{ cm}^3 \quad . \tag{32(c)}$$

P_o is the water pressure in atmospheres. These are the equations that will be used to estimate the performance of the main heat exchanger. They are the least accurate estimates in this report; exchangers with characteristics a factor of two or more better may be possible. However, they provide us with a beginning estimate.

The heat exchangers associated with the cooling of the H_2 and O_2 before compression are not as critical in design as the main exchanger. They involve a smaller flow rate and larger temperature differences between the two streams are tolerable. Consequently, we shall not discuss them in detail.

VI. PERFORMANCE OF A SAMPLE SYSTEM

There are so many variables and uncertainties in material parameters that it is not possible to design an optimum system at the present time. We can, however, pick reasonable values for the free parameters and find the performance of a system that will not deviate too greatly from the optimum system. We will first pick the most extreme conditions in terms of temperatures and water pressure under which the membranes may be expected to operate. After picking gas production pressures to give reasonable pumping requirements, the remaining parameters of the system will be determined by equations given earlier.

The values of parameters and reasons for picking them are as follows:

$T_1 = 1100^{\circ}K$ — Highest temperature possible avoiding excessive Pd loss rate

$T_2 = 1800^{\circ}K$ — Highest O_2 membrane temperature allowed

$P_o = 100$ atm — Most extreme conditions proposed for coal gasification processes[33]

$P_2 = 10^{-2}$ atm — To make pump costs reasonable

$P_{O_2} = 1.1 \times 10^{-2}$ atm — To provide pressure differential to drive O_2 through membrane

$X = 3.1 \times 10^{-4}$ — from Eqs. 6 and 9

$P_{H_2}(T_1) = 3.1 \times 10^{-2}$ — from $P_{H_2}(T_1) = XP_o$

$\varepsilon = 0.5$ — Reasonable to use half of energy immediately, store other half

$\Delta T = 2.34^{\circ}C$ — From Eq. 29

$A_{ex} = 8.3 \times 10^6 cm^2/K$ watt — Eq. 30 and 32(a) – area of heat exchanger for each K watt dissociation energy

$V = 5.45 \times 10^5 cm^3/K$ watt — Eq. 32(c)

$W_{ex} = 265$ watts/K watt — Eq. 32(b) Energy to drive heat exchanger

$t = 10^{-4}$ cm — Probably the thinnest membranes that can be built

$P_1 = 10^{-2}$ cm — Agreed pressure

$A_{H_2} = 39$ cm^2/K watt — Eq. 14 and above values for P_{H_2}, P_1 – area of H_2 membrane

$A_{O_2} = 1.5 \times 10^4 cm^2/K$ watt — Eq. 21 and above values for P_{O_2}, P_2 – area of O_2 membrane

The system as outlined here is quite clearly impractical for two reasons. First, the heat exchanger is too large and requires too much power to operate and second, the oxygen membrane is too large in area. Since the stabilized ZrO_2 membrane cannot operate above $1800^{o}K$, we are able to reduce the heat exchanger requirements only by increasing X and therefore decreasing the O_2 pressure, while we can reduce the size of the oxygen membrane only by increasing the O_2 pressure. We conclude that there is no way of making the membrane dissociation system based on a ZrO_2 oxygen membrane operate economically.

The development that would make the membrane dissociation scheme more attractive would be the discovery of a hydrogen membrane capable of operating at a temperature high enough to permit the condition $T_1 = T_2$ and therefore eliminate the heat exchanger. From Fig. 2, we see that a water pressure of 100 atm would require a membrane temperature of $1615^{o}K$ while a more reasonable water pressure of 10 atm requires $1860^{o}K$. The most likely candidate for such a membrane would be one of the compounds in Table II. The hydrogen permeability of these compounds should be measured. The possible use of membranes in a chemical cycle dissociation scheme should also be considered. Thus, even if the search for a membrane suitable for a membrane dissociation scheme is not successful, development of a very thin (10^{-4} cm) membrane is encouraged. A porous ceramic form covered with a thin film of palladium may well prove practical in this application.

REFERENCES

1. B. M. Abraham and F. Schreiner, Science 180, 959 (1973); Science 182, 1373 (1973).

2. G. deBeni and C. Marchetti, Enro Spectra 9, 46 (1970).

3. For a review of these techniques see the article by J. Shacter, E. Von Halle, and R. L. Hoglund in the Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Interscience Publishers, New York (1965), p. 91.

4. J. E. Funk and R. M. Reinstrom, I. and EC Progress, Design and Dev. 5, 336 (1966).

5. M. W. Zemansky, "Heat and Thermodynamics," 4th Edition, McGraw-Hill Book Company, Inc. New York (1957), p. 435.

6. S. T. Hsu, "Engineering Heat Transfer," Van Nostrand Company, Inc. Princeton, N. J. (1963) p. 212; Sisson and Pitts "Elements of Transport Phenomena," McGraw-Hill Book Company (1972). Chapter 13.

7. E. M. Wise, "Palladium Recovery Properties and Uses," Academic Press, New York (1968).

8. F. A. Lewis, "The Palladium-Hydrogen System," Academic Press, New York (1967).

9. The Englehard Industries Technical Bulletin VII, (1966) pp. 9-62.

10. J. G. E. Cohn, US Patent 3, 238, 700.

    H. K. Straschil and T. C. Lopez, US Patents 3, 238, 703; 3, 238, 704.

    W. C. Pfefferle, US Patent 3, 241, 293.

    R. E. Bonnet, US Patent 3, 245, 206.

    G. G. Pinney and H. G. Hempill, US Patent 3, 226, 915.

    D. L. McKinley, US Patents 3, 232, 026; 3, 247, 648.

    J. B. Hunter, US Patent 3, 254, 956.

11. G. L. Matlack, Platinum Metals Review 13, 26 (1969).

    P. M. Roberts and D. A. Stiles, Pt. Metals Rev. 13, 141 (1969).

12. W. P. Davis, USAEC Report KAPL-1227, U.S. Atomic Energy Commission Washington, D.C. (1954).

13. G. Toda, J. Res. Inst. Catalysis, Hokkaido Univ. 6, 13 (1958).

14. A. de Rosset, J. Ind. Eng. Chem. 52, 525 (1960).

15. R. C. Hurlbert and J. O. Konecny, J. Chem. Phys. 34, 655 (1961).

16. A. C. Makrides and D. N. Jewett, Ref. 9, p. 51.

17. L. R. Rubin, Ref. 9, p. 55.

18. O. M. Katz and E. A. Gulbrausen, Rev. Sci. Instr. 31, 615 (1960).

19. A. N. Nesmeyanov "Vapor Pressure of the Elements," Academic Press, New York (1963).

20. O. Loebich, Jr. and E. Raub, J. of the Less Common Metals 30, 47 (1973).

21. A. W. Smith, F. W. Meszaros, and C. D. Amata, J. Am. Ceramic Soc. 49, 240 (1966).

22. C. B. Alcock and J. C. Chan, Canadian Metallurgical Quarterly 11, 559 (1972).

22a. C. A. Alexander, J. S. Ogden, and G. W. Cunningham, Battelle Memorial Institute Report BMI-1789 (1967).

22b. R. Ackermann, Private communication.

23. K. W. Lay, J. Am. Ceramic Soc. 53, 369 (1970).

24. A. M. Anthony, R. Kiyoura, and T. Sata, J. of Nuclear Materials 10, 8 (1963).

25. K. Hagemark and M. Broli, J. Inorg. Nucl. Chem. 28, 2837 (1966).

26. R. J. Thorn and G. H. Winslow, J. Chem, Phys. 44, 2822 (1966).

27. J. Belle, J. Nuclear Materials 30, 3 (1969).

28. J. F. Marin and P. Contamin, J. Nuclear Materials 30, 16 (1969).

29. K. W. Lay, J. Am. Ceramic Society, 53, 369 (1970).

30. P. E. Blackburn, J. Nuclear Materials 46, 244 (1973).

31. W. M. Kays, A. L. London, and D. W. Johnson, "Gas Turbine Plant Heat Exchangers," ASME publication (1951).

32. W. H. McAdams, "Heat Transmission," McGraw-Hill Book Company Inc., New York (1954).

33. R. E. Dial, "Refractories for Coal Gasification," Paper presented at Canadian Ceramic Society Meeting, Montreal, Quebec, Canada, 25 Feb. 1974, and at American Ceramic Society Meeting, Chicago, Ill. on 30 April 1974.

/